Dynamics and Kinetics. Exercises 11-12: Solutions

Problem 1

We want to use the TST to estimate the rate constant for the reaction H + HBr → H_2 + Br.
We know from the class that

$$k_{\mathrm{TST}} = N_{\mathrm{Av}} \frac{k_{\mathrm{B}}T}{h} \frac{q_V^{\ddagger}}{q_{V,\mathrm{H}} q_{V,\mathrm{HBr}}} \mathrm{e}^{-\epsilon^0/k_{\mathrm{B}}T} = N_{\mathrm{Av}} \frac{k_{\mathrm{B}}T}{h} \frac{\tilde{q}_V^{\ddagger}}{\tilde{q}_{V,\mathrm{H}} \tilde{q}_{V,\mathrm{HBr}}} \mathrm{e}^{-\epsilon^0_{\mathrm{QM}}/k_{\mathrm{B}}T}.$$

See Fig. 2.

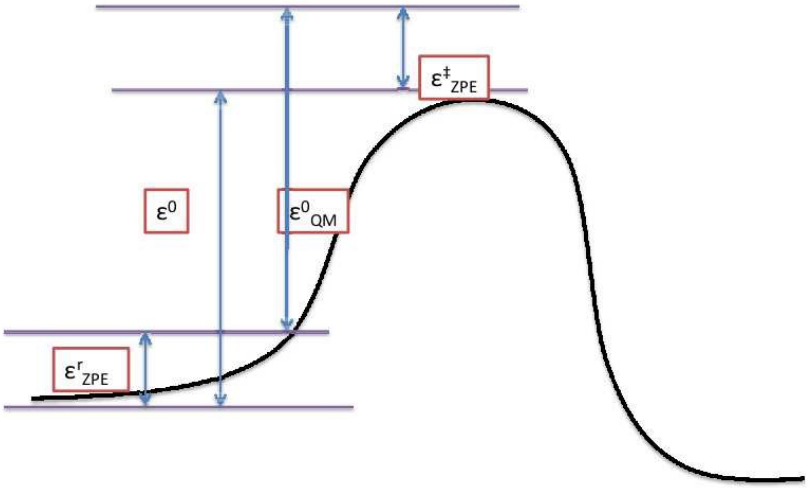

Figure 1: Transition state

(1) First of all we consider the **reactants**: H + HBr.

Masses:

$$m_{\mathrm{H}} = 1.674 \times 10^{-27}\mathrm{kg},$$
$$m_{\mathrm{HBr}} = \frac{M_{\mathrm{H}} + M_{\mathrm{Br}}}{N_{\mathrm{Av}}} = \frac{(1.008 + 79.92) \times 10^{-3}}{6.022 \times 10^{23}}\mathrm{kg} = 1.338 \times 10^{-25}\mathrm{kg}.$$

Moment of inertia of HBr:

$$I = \mu d^2 = \frac{m_{\mathrm{H}} \cdot m_{\mathrm{Br}}}{m_{\mathrm{H}} + m_{\mathrm{Br}}} d^2_{\mathrm{HBr}} = 1.674{\times}10^{-27}\mathrm{kg}{\times}\frac{79.92}{1.008 + 79.92}{\times}(1.414{\times}10^{-10})^2\mathrm{m}^2 = 3.306{\times}10^{-47}\mathrm{kg\,m}^{-2}.$$

(2) Now, let us consider the **collinear transition state** H···H···Br:
Mass:

$$m_{\ddagger} = 2m_{\mathrm{H}} + m_{\mathrm{Br}} = 1.37 \times 10^{-25}\mathrm{kg}.$$

Center of mass (see Fig. 3):

$$m_{\mathrm{H}}x + m_{\mathrm{H}}(x-150) = m_{\mathrm{Br}}(150+142-x) \Rightarrow x = \frac{m_{\mathrm{Br}}\times 292 + m_{\mathrm{H}}\times 150}{2m_{\mathrm{H}}+m_{\mathrm{Br}}} = 283.3 \text{ pm}.$$

Therefore the moment of inertia is

$$I^{\ddagger} = (m_{\mathrm{H}}\times 283.3^2 + m_{\mathrm{H}}\times 133.3^2 + m_{\mathrm{Br}}\times 8.7^2)\mathrm{pm}^2 = 1.74\times 10^{-46}\mathrm{kg\ m}^2.$$

(3) It is now possible to compute the **partition functions**:

For the **H atom** we have

$$\tilde{q}_{V,\mathrm{H}} = q_{V,\mathrm{H}} = q_{V,\mathrm{H,tr}} = \left(\frac{2\pi m_{\mathrm{H}} k_{\mathrm{c}} T}{h^3}\right)^{3/2} = 9.90\times 10^{29}\mathrm{m}^{-3}.$$

For **molecule HBr** we have

$$\tilde{q}_{V,\mathrm{HBr}} = q_{V,\mathrm{HBr,tr}} q_{\mathrm{HBr,rot}} \tilde{q}_{\mathrm{HBr,vib}},$$

where $q_{V,\mathrm{HBr,tr}}$ and $q_{\mathrm{HBr,rot}}$ do not have a ZPE (it is exactly zero), while we get $\tilde{q}_{\mathrm{HBr,vib}}$ by measuring energies from the ZPE levels:

$$q_{V,\mathrm{HBr,tr}} = \left(\frac{2\pi m_{\mathrm{HBr}} k_{\mathrm{B}} T}{h^3}\right)^{3/2} = 7.10\times 10^{32}\mathrm{m}^{-3},$$
$$q_{\mathrm{HBr,rot}} = \frac{8\pi^2 I_{\mathrm{HBr}} k_{\mathrm{B}} T}{h^2} = 24.6,$$
$$q_{\mathrm{HBr,vib}} = \frac{1}{1-\mathrm{e}^{-x}} \approx 1 \quad \text{since} \quad x = \frac{h\tilde{\nu}c}{k_{\mathrm{B}}T} = 12.7.$$

Hence

$$\tilde{q}_{\mathrm{V,HBr}} = 7.10\times 10^{32}\mathrm{m}^{-3}\times 24.6\times 1 = 1.75\times 10^{34}\mathrm{m}^{-3}.$$

For the **transition state** H···H···Br we have

$$\tilde{q}^{\ddagger}_{\mathrm{V}} = q^{\ddagger}_{\mathrm{V,tr}} q^{\ddagger}_{\mathrm{rot}} \tilde{q}^{\ddagger}_{\mathrm{vib}},$$

where $q^{\ddagger}_{v,\mathrm{tr}}$ and $q^{\ddagger}_{rot,\mathrm{t}}$ q^{V} do not have a ZPE (it is exactly zero), while we get $\tilde{q}^{\ddagger}_{vib,}$ by measuring energies from the ZPE levels. It is now easy to compute the quantities that we need:

$$q^{\ddagger}_{\mathrm{V,tr}} = \left(\frac{2\pi m_{\ddagger} k_{\mathrm{B}} T}{h^3}\right)^{3/2} = 7.32\times 10^{32}\mathrm{m}^{-3},$$
$$q^{\ddagger}_{\mathrm{rot}} = \frac{8\pi^2 I^{\ddagger} k_{\mathrm{B}} T}{h^2} = 129.7.$$

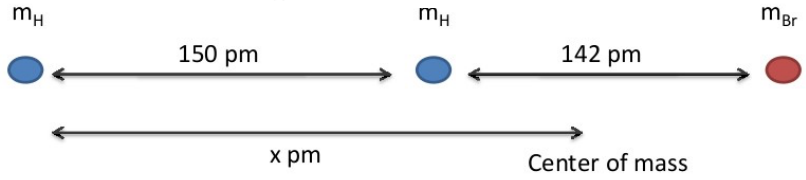

Figure 2: Center of mass

Since $x_{\mathrm{SS}} = \frac{hc\tilde{\nu}_{\mathrm{SS}}}{k_{\mathrm{B}}T} = 11.2$ and $x_{\mathrm{bend}} = \frac{hc\tilde{\nu}_{\mathrm{bend}}}{k_{\mathrm{B}}T} = 2.19$, we get

$$\tilde{q}^{\ddagger}_{\mathrm{vib}} = \frac{1}{(1-\mathrm{e}^{-x_{\mathrm{SS}}})\,(1-\mathrm{e}^{-x_{\mathrm{bend}}})^2} = 1.27$$

.

Altogether, the TS partition function is

$$\tilde{q}^{\ddagger}_{\mathrm{V}} = 7.32 \times 10^{32}\mathrm{m}^{-3} \times 129 \times 7 \times 1.27 = \ 1.21 \times 10^{35}\mathrm{m}^{-3}$$

.

(4) Collecting all the intermediate results for partition functions, the TST rate constant is finally

$$\begin{aligned} k_{\mathrm{TST}} &= N_{\mathrm{Av}} \frac{k_{\mathrm{B}}T}{h} \frac{\tilde{q}^{\ddagger}_{\mathrm{V}}}{\tilde{q}_{\mathrm{V,H}}\tilde{q}_{\mathrm{V,HBr}}} e^{-\epsilon^0_{\mathrm{QM}}/k_{\mathrm{B}}T} \\ &= 6.02 \times 10^{23} \frac{1.38 \times 10^{-23} \times 300}{6.53 \times 10^{-34}} \frac{1.21 \times 10^{35}}{9.9 \times 10^{29} \times 1.75 \times 10^{34}} e^{-5000/(8.314\times 300)} \mathrm{m}^3\mathrm{s}^{-1}\mathrm{mol}^{-1} \\ &= 3.54 \times 10^{6}\mathrm{m}^3\mathrm{mol}^{-1}\mathrm{s}^{-1} = 3.54 \times 10^{9}\mathrm{M}^{-1}\mathrm{s}^{-1}. \end{aligned}$$

Problem 2

$$q^{\ddagger}_{v,\mathrm{tr}} = 10^{32}\mathrm{m}^{-3}$$

$$q^{\ddagger}_{rot} = 10$$

$$\tilde{\mathrm{q}}^{\ddagger}_{vib} = 1$$

$A + B\text{—}C \rightarrow A\text{- -}B\text{- -}C \rightarrow$ products

Reactants:

$qV,A = qV,tr$ *[atom: only translations]*

$q_{V,B} = q_{V,\mathrm{tr}}\mathrm{q}^2_{\mathrm{rot}}\mathrm{q}_{\mathrm{vib}}$ b [diatom: 3 translations, 2 rotations, 1 vibration.]

Transition state:

$$q^{\ddagger}_{V} = q^{\ddagger}_{V,\mathrm{tr}} q^2_{\mathrm{rot}} q^{3N-6=3}_{\mathrm{vib}}$$

Explanation: It is a linear molecule so we have 3 translations, 2 rotations, $3N-5$ vibrations, but 1 vibration becomes reaction coordinate! ⇒ $3N-6$ vibrations remain in the transition state.

Rate constant

$$\begin{aligned} k_{\mathrm{TST}} &= N_{\mathrm{Av}} \frac{k_B T}{h} \frac{q^{\ddagger}_{V}}{q_{V,A} q_{V,B}} e^{-\varepsilon^0/k_B T} \\ &= N_{\mathrm{Av}} \frac{k_B T}{h} \frac{q_{V,\mathrm{tr}} q^2_{\mathrm{rot}} q^3_{\mathrm{vib}}}{q_{V,\mathrm{tr}} q_{V,\mathrm{tr}} q^2_{\mathrm{rot}} q_{\mathrm{vib}}} e^{-\varepsilon^0/k_B T} \\ &= N_{\mathrm{Av}} \frac{k_B T}{h} \frac{q^2_{\mathrm{vib}}}{q_{V,\mathrm{tr}}} e^{-\varepsilon^0/k_B T} \end{aligned}$$

We are given $\tilde{q}_{vib} = 1$, not q_{vib}.

Since $q_{vib} = e^{-\frac{1}{2}h\nu/k_BT}\tilde{q}_{vib}$, we have

$$k_{\mathrm{TST}} = N_{\mathrm{Av}} \frac{k_B T}{h} \frac{\tilde{q}^2_{\mathrm{vib}}}{q_{V,\mathrm{tr}}} e^{-\varepsilon^0_{\mathrm{QM}}/k_B T}$$

where

$$\varepsilon^0_{\mathrm{QM}} = \varepsilon^0 + 2 \times \frac{1}{2} h\nu = \varepsilon^0 + \varepsilon^0_{\mathrm{ZPE}}$$

Pre-exponential factor is

$$\begin{aligned} f &= N_{\mathrm{Av}} \frac{k_B T}{h} \frac{\tilde{q}^2_{\mathrm{vib}}}{q_{V,\mathrm{tr}}} = \frac{RT}{h} \frac{1^2}{10^{32}\mathrm{m}^{-3}} = \frac{8.314 \times 300 \times 10^{-32}}{6.63 \times 10^{-34}} \mathrm{m}^3\mathrm{mol}^{-1}\mathrm{s}^{-1} \\ &= 3.76 \times 10^7 \mathrm{dm}^3\mathrm{mol}^{-1}\mathrm{s}^{-1} \end{aligned}$$

Problem 3

Given the reaction $H_2 + D_2 \rightarrow 2HD$, the equilibrium constant is:

$$K_{\mathrm{eq}} = \frac{q^2_{V,\mathrm{HD}}}{q_{V,\mathrm{H_2}} q_{V,\mathrm{D_2}}}.$$

Note that in this case $K_{eq} = K_N = K_p = K_c = K_p$ since $\Delta\nu = \nu_{H2} + \nu_{D2} + \nu_{HD} = -1 - 1 + 2 = 0$.
The partition functions per unit volume for H_2, D_2 and HD are:

$$q_{V,\mathrm{H_2}} = q_{V,\mathrm{tr}} \times q_{\mathrm{rot}} \times q_{\mathrm{vib}} = \frac{(2\pi k_B T)^{3/2}}{h^3} \cdot m_{\mathrm{H_2}}^{3/2} \times \overbrace{\frac{1}{2}}^{\text{Symetry factor}} \frac{8\pi^2 k_B T}{h^2} \cdot I_{\mathrm{H_2}} \times \frac{e^{-\frac{x_{\mathrm{H_2}}}{2}}}{1-e^{-x_{\mathrm{H_2}}}}$$

$$q_{V,\mathrm{D_2}} = q_{V,\mathrm{tr}} \times q_{\mathrm{rot}} \times q_{\mathrm{vib}} = \frac{(2\pi k_B T)^{3/2}}{h^3} \cdot m_{\mathrm{D_2}}^{3/2} \times \frac{1}{2} \frac{8\pi^2 k_B T}{h^2} \cdot I_{\mathrm{D_2}} \times \frac{e^{-\frac{x_{\mathrm{D_2}}}{2}}}{1-e^{-x_{\mathrm{D_2}}}}$$

$$q_{V,\mathrm{HD}} = q_{V,\mathrm{tr}} \times q_{\mathrm{rot}} \times q_{\mathrm{vib}} = \frac{(2\pi k_B T)^{3/2}}{h^3} \cdot m_{\mathrm{HD}}^{3/2} \times \frac{8\pi^2 k_B T}{h^2} \cdot \underbrace{I_{\mathrm{HD}}}_{=r^2\mu_{\mathrm{HD}}} \times \frac{e^{-\frac{x_{\mathrm{HD}}}{2}}}{1-e^{-x_{\mathrm{HD}}}},$$

where $I = \mu r^2$ and $x := \frac{h\nu}{k_B T}$. Substituting the translational and rotational partition functions in the expression for K_{eq}, we find

$$K_{\mathrm{eq}} = \left(\frac{m_{\mathrm{HD}}^2}{m_{\mathrm{H_2}} m_{\mathrm{D_2}}}\right)^{3/2} \times 4 \frac{\mu_{\mathrm{HD}}}{\mu_{\mathrm{H_2}} \mu_{\mathrm{D_2}}} \times \frac{q_{\mathrm{vib,HD}}^2}{q_{\mathrm{vib,H_2}} q_{\mathrm{vib,D_2}}}.$$

Note that many terms in the translational and rotational partition functions cancel out. In particular, in the Born-Oppenheimer approximation, the bond length r is the same for the 3 molecules. Let us compute the required ingredients:

- $m_{\mathrm{H_2}} = 2m_{\mathrm{H}}, \quad m_{\mathrm{D_2}} = 2m_{\mathrm{D}}, \quad m_{\mathrm{HD}} = m_{\mathrm{H}} + m_{\mathrm{D}}$
- $\mu_{\mathrm{H_2}} = \frac{m_{\mathrm{H}} m_{\mathrm{H}}}{m_{\mathrm{H}} + m_{\mathrm{H}}} = \frac{m_{\mathrm{H}}}{2}, \quad \mu_{\mathrm{D_2}} = \frac{m_{\mathrm{D}} m_{\mathrm{D}}}{m_{\mathrm{D}} + m_{\mathrm{D}}} = \frac{m_{\mathrm{D}}}{2}, \quad \mu_{\mathrm{HD}} = \frac{m_{\mathrm{H}} m_{\mathrm{D}}}{m_{\mathrm{H}} + m_{\mathrm{D}}}$
- $x_{\mathrm{H_2}} = 20.99, \quad x_{\mathrm{D_2}} = 14.85, \quad x_{\mathrm{HD}} = 18.18$
- $q_{\mathrm{vib,H_2}} = 2.77 \times 10^{-5}, \quad q_{\mathrm{vib,D_2}} = 5.97 \times 10^{-4}, \quad q_{\mathrm{vib,HD}} = 1.13 \times 10^{-4},$

Substituting the ingredients and using the fact that $m_{\mathrm{D}} \cong 2m_{\mathrm{H}}$, we find:

$$\begin{aligned} K_{\mathrm{eq}} &= \frac{(m_{\mathrm{H}} + m_{\mathrm{D}})^3}{(4 m_{\mathrm{H}} m_{\mathrm{D}})^{3/2}} 4 \frac{(m_{\mathrm{H}} m_{\mathrm{D}})^2 4}{(m_{\mathrm{H}} + m_{\mathrm{D}})^2 m_{\mathrm{H}} m_{\mathrm{D}}} \frac{q_{\mathrm{vib,HD}}^2}{q_{\mathrm{vib,H_2}} q_{\mathrm{vib,D_2}}} \\ &= 4 \frac{(m_{\mathrm{H}} + m_{\mathrm{D}})}{2(m_{\mathrm{H}} m_{\mathrm{D}})^{1/2}} \frac{q_{\mathrm{vib,HD}}^2}{q_{\mathrm{vib,H_2}} q_{\mathrm{vib,D_2}}} = \underbrace{4}_{\text{symmetry}} \times \underbrace{\frac{3}{2 \cdot 2^{1/2}}}_{\substack{\text{mass effects} \\ \text{(trans. and rot.)}}} \times \underbrace{\frac{(1.13 \times 10^{-4})^2}{2.77 \times 10^{-5} \cdot 5.97 \times 10^{-4}}}_{\text{mostly ZPE}} = 3.266 \end{aligned}$$

Problem 4

Reaction 1: $E_{a1} = E_a$, $\Delta S_1^{\ddagger\circ}$;
Reaction 2: $E_{a2} = E_{a1} = E_a$, $\Delta S_2^{\ddagger\circ} = \Delta S_1^{\ddagger\circ} + 50 \mathrm{JK^{-1}mol^{-1}}$
Using the general thermodynamic formulation of TST for a reaction of any order, we have

$$k_{\mathrm{TST}} = \frac{k_B T}{h} (c^\circ)^{\Delta n^\ddagger} e^{-\Delta G^{\ddagger\circ}/RT} = \frac{k_B T}{h} (c^\circ)^{\Delta n^\ddagger} e^{\Delta S^{\ddagger\circ}/R} e^{-\Delta H^{\ddagger\circ}/RT}$$

where $c^\circ = 1\text{mol}\cdot\text{dm}^{-3}$ is the standard-state molar concentration.
Relating TST to the Arrhenius law by setting

$$k_{\text{TST}} = Ae^{-Ea/RT} \tag{1}$$

we found that the activation energy is related to the standard enthalpy of activation by

$$E_a = \Delta H^{\ddagger\circ}_{\ddagger} + (1 - \Delta n^{\ddagger}_{\ddagger})RT$$

with the pre-exponential factor

$$A = \frac{k_B T}{h}(c^\circ)^{\Delta n^\ddagger} e^{-(\Delta n^\ddagger - 1)} e^{\Delta S^{\ddagger\circ}/R} \tag{2}$$

Considering that the reactions are of the same order, i.e., $\Delta n^{\ddagger}_{\ddagger}$ is the same in both cases, the ratio of the rate constants is:

$$\frac{k_{\text{TST},2}}{k_{\text{TST},1}} \overset{(1)}{=} \frac{A_2 e^{-E_a/RT}}{A_1 e^{-E_a/RT}} \overset{E_{a1}=E_{a2}}{=} \frac{A_2}{A_1} \overset{(2)}{=} e^{(\Delta S^{\ddagger\circ}_2 - \Delta S^{\ddagger\circ}_1)/R} = e^{50/8.314} = 409.$$

Problem 5

We know $k_{\text{TST}} = 2.34 \times 10^{-2}\text{dm}^3\text{mol}^{-1}\text{s}^{-1}$, $E_a = 150\text{kJ/mol}$, and that the order of reaction n=2

- $\Delta G^{\ddagger\circ}_{\ddagger}$: From TST:

$$k_{\text{TST}} = \frac{k_B T}{h}(c^\circ)^{1-n} e^{-\Delta G^{\ddagger\circ}/RT}$$

  where $c^\circ = 1\text{mol}\cdot\text{dm}^{-3}$ is the standard-state molar concentration (note that it is necessary to keep consistency in the units).

$$\Delta G^{\ddagger\circ} = -RT\ln\left(\frac{k_{\text{TST}} h c^\circ}{k_B T}\right) = 190.4\text{kJ/mol}$$

- $\Delta H^{\ddagger\circ}_{\ddagger}$: From the expression for the activation energy:

$$E_a = \Delta H^{\ddagger\circ}_{\ddagger} + (1 - \Delta n^{\ddagger}_{\ddagger})RT; \qquad \Delta n^{\ddagger}_{\ddagger} = n^{\ddagger}_{\ddagger} - n_{\text{react}} = 1 - 2 = -1$$

  (since there are two molecules of reactants and 1 molecule of TST)

$$\Delta H^{\ddagger\circ}_{\ddagger} = E_a - 2RT = 138.8\text{kJ/mol}$$

- $\Delta S^{\ddagger\circ}_{\ddagger}$: We know that

$$G = H - TS \qquad \Rightarrow \Delta S^{\ddagger\circ} = \frac{\Delta H^{\ddagger\circ} - \Delta G^{\ddagger\circ}}{T} = -76.6\,\text{J}\cdot\,\text{mol}^{-1}\cdot\text{K}^{-1}$$

- A: From $k_{\text{TST}} = Ae^{-E_a/RT}$ we easily find that

$$A = k_{\text{TST}} e^{E_a/RT} = 1.03 \times 10^{10}\text{M}^{-1}\text{s}^{-1}$$